PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08J 9/32, C08K 3/40, B27N 3/00

A1

(11) International Publication Number: WO 99/18150

(43) International Publication Date: 15 April 1999 (15.04.99)

(21) International Application Number: PCT/US98/20998

(22) International Filing Date: 7 October 1998 (07.10.98)

(30) Priority Data:
60/061,539 7 October 1997 (07.10.97) US
09/169,803 6 October 1998 (06.10.98) US

(71) Applicant: QUESTECH CORPORATION [US/US]; 1197 Exchange Street, Middlebury, VT 05753 (US).

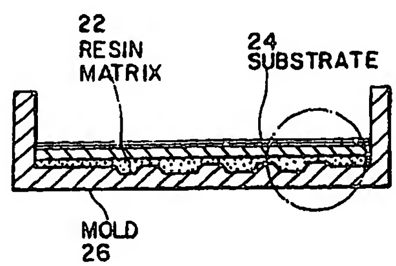
(72) Inventors: QUESTEL, Roger; R.R. 1, Box 2120, Sandgate Road, Arlington, VT 05250 (US). PELLETIER, David; 1010 Fern Lake Road, Brandon, VT 05733 (US). MERRIAM, Brent; P.O. Box 694, East Middlebury, VT 05740 (US).

(74) Agents: LAWRENCE, William, F. et al.; Frommer Lawrence & Haug LLP, 745 Fifth Avenue, New York, NY 10151 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: IN MOLD BONDED THIN COMPOSITES AND A METHOD FOR MANUFACTURING THE COMPOSITES



(57) Abstract

This invention relates to a decorative and/or architectural composite article fabricated from a resin matrix (22) bound to a substrate (24). The resin matrix (22) primarily contains a curable liquid resin, metal or stone particles, and a catalyst. The composite piece has the appearance of metal or stone and the utility of a peace of plywood, particle board, or other building panel. This invention also relates to a process for fabricating the composite pieces. In addition, this invention is directed to a thin, composite sheet or laminate-like product and methods for manufacturing the thin composite. This thin composite has the appearance of metal or stone, but can be used in construction like a piece of high-pressure decorative laminate or flexible paneling or the like.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

TITLE OF THE INVENTION

IN MOLD BONDED THIN COMPOSITES AND A METHOD FOR MANUFACTURING THE COMPOSITES

FIELD OF THE INVENTION

This invention relates generally to the production of utilitarian or decorative architectural objects. The objects are composite pieces formed from a resin matrix containing metal or stone particles (or powders) bonded by curing the liquid resin matrix on a substrate so that the hardened matrix is bonded to the substrate without an intermediate adhesive. The resultant composite has the physical appearance of metal or stone but can be used in construction like a piece of sheet rock, panelling, plywood, particle board or the like. More specifically, the architectural objects of this invention are composite pieces formed from a polymerized resin matrix containing metal or stone particles (or powders) to which a thin substrate is bonded. The resultant composite has the physical appearance of metal or stone, but can be used in construction like a piece of high-pressure decorative laminate or flexible paneling or the like.

BACKGROUND OF THE INVENTION

One way of imparting a metallic or stone-like appearance to an object is, of course, to cast that object from the metal or carve it in stone. However, casting an object from metal such as bronze or copper can be a relatively expensive process with the result that decorative and architectural objects such as panels, tiles and the like are not readily available in the mass market to ordinary consumers.

Attempts have been made in the past to impart a bronze-like appearance to decorative or utilitarian objects. However, these objects generally do not have the appearance of a genuine bronze or a metallic body. For instance, ceramic objects such as floor and wall tiles have been glazed with a coating of metallized enamel. It is also possible to create a thin metallized surface by vacuum deposition, sputtering or other plating techniques on the face of a plastic body.

U.S. Patent No. 2,454,910 to Carr discloses a molding technique in which the surface of the mold is coated with a bronzing liquid in which bronze particles are dispersed in a resin base to create a bronze-like layer in the mold which is then filled with a moldable plastic material such as phenolic.

U.S. Patent No. 3,615,963 to Johansson et al. discloses a technique for producing a reinforced panel by spreading a mixture of a liquid resinous binder and solid particles of sand or metal powder on a stainless steel base treated with a release agent, the particles settling and concentrating adjacent the base plate.

In U.S. Patent No. 2,773,287 to Stout, a reinforced plastic pipe is disclosed in which glass fibers, crushed rock or other non-metallic particles are mixed with a polyester resin and added to a pipe mold which is then rotated to produce a centrifugal force causing the particles to migrate toward the outer surface of the tube.

U.S. Patent No. 5,171,497 to Osada relates to a method for manufacturing a building panel by providing a base sheet with an adhesive, applying small stones (or crushed ceramics) to the base sheet so that the stones adhere to the base sheet, applying a water absorbing polymer to the stones and the spaces in between the stones on the base sheet, spreading an inorganic hardening material (e.g. cement) over the stones and drying the hardening material. According to this process,

the polymer absorbs water from the hardening material and expands to prevent the stones from being buried in the hardening material.

U.S. Patent No. 4,714,623 to Riccio et al. relates to a method of metal cladding a surface by applying a curable adhesive layer (e.g. epoxy resin) to the surface, spraying a layer of hollow glass, ceramic or carbon microspheres to the adhesive layer, curing the adhesive layer, rupturing the surface materials to produce a matrix of undercuts over the surface, and thermally spraying metal in molten particles to form a metal layer. According to this process, the bond between the metal coating and the substrate surface increases due to the formation of the matrix of undercuts created by abrading the surface materials which are sprayed on the surface of the substrate.

U.S. Patent No. 5,177,124 and U.S. Patent No. 5,280,052 to Questel et al. relate to a process for making a plastic/metal matrix material and objects formed from the material. Using the process described in the patents, a mixture of a liquid plastic monomer, a curing agent, a dispersion of metal particles, and a dispersion of floatable particles (such as glass or ceramic microspheres) are poured into a mold. The metal particles settle in the mold to the lower surface of the piece or the mold is centrifuged to cause the metal particles to migrate toward the outer region of the piece before the monomer polymerizes and hardens. The floatable particles rise to the upper or inner surface of the object. As the liquid monomer cures and shrinks, the presence of the metallic particles at one surface of the object and the floatable particles at the opposing surface ensure that the monomer will shrink evenly and maintain the desired shape. After removal from the mold, the outer face of the piece is polished. The plastic/metal matrix material described in these patents uses small amounts of metal in proportion to the resin. The plastic/metal matrix also includes

floatable particles as a means for preventing uneven shrinkage of the resin matrix. These patents do not teach or describe a method for bonding the resin matrix to the substrate or the resulting composite article.

There are other processes for applying metallic coatings to substrates. These include physical vapor deposition processes including vacuum evaporation, sputter deposition, ion plating, laminating of metal and metallic foils, electroless plating, and electroplating. However, there are a number of disadvantages associated with each of these techniques. Electroplating requires waste treatment of plating solutions and the use of alkaline cyanides and acids. In addition, there are strong and dangerous odors from certain types of plating solutions. Vacuum evaporation can not be used for many types of alloys and compounds and high radiant heat loads can be utilized in the deposition system. Further, there is often poor surface coverage on complex surfaces and poor film thickness uniformity over large surfaces using the vacuum evaporation method. With sputter deposition, sputtering rates are low compared to thermal evaporation. Additionally, sputtering targets are often expensive and material utilization may be poor. Moreover, gaseous contaminants are activated in the plasma and radiation and bombardment from the sputtering target can degrade the substrate.

In the boating industry, boat hulls are often fabricated from fiberglass embedded in resins. In order to enhance the structural integrity of certain parts, such as gasoline tank covers, the fiberglass resin can be reinforced with a piece of plywood. The gasoline tank covers can be formed by adding a fiberglass-containing resin into a mold in the shape of a cover, placing a piece of plywood in the mold, and adding additional fiberglass-containing resin to the back of the plywood to encase the plywood. The technique is used to enhance the structural qualities of the fiberglass-containing resin. The technique uses a thick layer of fiberglass and resin to

prevent "print-through", that is, to prevent the substrate surface from showing through the surface of the fiberglass and resin. The surface can be treated by polishing or buffing it.

A company, Forms + Surfaces, in California markets a product made from metal particles, resin and unhardened fiberglass matte. It appears that the resin and particles are sprayed into molds followed by immersion or embedding an unhardened fiberglass matte in the resin and particles. Warpage is a significant problem and a genuine metallic appearance is not achieved.

U.S. Patent No. 5,393,568 to Valente et al. discloses a cold process for laying a textured or polished coat of bronze, copper, brass, pewter or other metallic substance over a mineral or organic surface comprising the step of mixing a sintering metal powder with a polyester resin and a ketonic catalyst for forming a spreadable, moldable, or sprayable past that hardens to a coat having essentially the mechanical and chemical characteristics of the selected metallic substance, but exhibiting no electrical conductivity. Detailed textures cannot be achieved with this method as design details of the substrate materials are muted by the application of the spray metal coating. In addition, by gravity, the metal particles migrate towards the surface of the object onto which they are coated.

Axolotl Metal Finishes of Australia consist of a liquid application which utilizes real metals and is applied to form a veneer on a variety of building materials of varying shapes and size. Detailed textures cannot be achieved with this method as design details of the substrate materials are muted by the application of the spray metal coating.

The present invention provides a distinct improvement over the prior art. None of the prior art references describe a composite which has the appearance of

stone or metal and that can be used in construction like a piece of a board-like material such as plywood or other structural surface. None of the prior art references describe a composite which has the appearance of stone or metal and that can be used in construction like a piece of high pressure decorative laminate, thin paneling or the like. Nor does the art teach a process for making the composite piece. The resin matrix of the present invention generally utilizes a thin layer of resin matrix on the substrate, contains a high ratio of metal or stone particles to liquid resin, and does not require the presence of floatable particles or microspheres. Furthermore, the surface of the composite of the invention can be provided with graphic details, relief patterns and designs. In addition, the invention, after proper finishing, has a metallic or stone outer face which imparts the appearance of a solid metal casting or carved or natural stone surface. Moreover, the present invention permits the manufacture of bonded composite structures in which a metal matrix material is adhered directly to a substrate without the need for an intermediate adhesive.

OBJECTS OF THE INVENTION

An object of this invention is to provide a decorative and/or architectural composite article fabricated primarily from a resin matrix containing a curable liquid resin, metal or stone particles (or powder) and a catalyst bonded to a substrate. The composite article has the appearance of metal or stone, and has the utility of a piece of wood, plywood, particle board, wood laminate, honeycomb, metal, medium density fiberboard (MDF), concrete, gypsum board, plastic or other structural surface.

Another object of this invention is to produce a composite article having the appearance of metal or stone, and having the utility of a piece of high pressure decorative laminate, thin paneling or the like.

It is a further object of this invention to provide a decorative/architectural composite article in which the resin matrix is bonded to the substrate without the use of an intermediate adhesive.

It is another object of this invention to provide a process for creating a bonded composite having a curable resin matrix attached to a substrate, wherein the resin matrix is cured to bond the inner surface to the substrate and to form a metallic or stone surface on the outer surface which gives the piece the appearance of a metal or stone object.

It is yet another object of this invention to provide a method for fabricating the composite pieces which are composed of resin matrix and metal or stone particles substantially attached to a substrate.

It is still another object of this invention to provide a method for fabricating the composite pieces which are composed of a matrix of a curable liquid resin, a catalyst, metal or stone particles and, optionally, floatable particles attached to a substrate.

It is a further object of the invention to provide method which lends itself to mass production at relatively low cost to fabricate the composite pieces.

SUMMARY OF THE INVENTION

The objects of the invention are attained in a process for forming a utilitarian or decorative composite piece fabricated primarily of a resin matrix bonded directly, without an intermediate adhesive, to a thin substrate. The composite product

has the hand and appearance of genuine metal or stone on the face and the ability to be utilized in construction as a piece of architectural plywood or other board-like substance or a high pressure decorative laminate, thin paneling or the like. However, if desired, it can be significantly lighter in weight than an actual metal or stone panel.

The resin matrix is a mixture of a curable liquid resin, a curing agent (catalyst) therefor, and a dispersion of metal or stone particles (or powder) which are more dense than the liquid resin. Alternately, the resin matrix is a mixture of a liquid resin curable by heat or heat and pressure, and a dispersion of metal or stone particles (or powder) which are more dense than the liquid resin. The resin matrix can optionally contain floatable particles which are less dense than the curable liquid resin.

This invention also relates to a process for manufacturing the composite articles including a polymerized resin matrix containing metal or stone particles bonded to a thin substrate. The resin matrix has an outer surface which provides a metallic or stone-like appearance to the composite and an inner surface which is in contact with and binds to the substrate without the use of an adhesive. The process of fabricating the composite comprises the steps of combining a curable liquid resin, a catalyst, and particles; pouring the resin matrix into a mold; introducing the substrate into the mold to contact a surface of the substrate with the resin matrix; forming a concentrated mass of the particles on the outer surface of the resin matrix (away from the surface of the substrate that is in contact with the resin matrix) by migration of the particles to the outer surface of the resin matrix before curing of the resin matrix; curing the resin matrix so that the resin matrix is bonded to the substrate by curing to create the bonded composite. The bonded composite can be removed from the mold and subjected to a post-curing process such as heat.

More specifically, the process of fabricating the composite comprises the steps of combining a liquid curable resin, a catalyst or curing agent, and metal or stone particles; spraying or brushing a thin layer of the resin matrix into a mold; forming a concentrated mass of metal or stone particles on the surface of the mold; curing the resin matrix; combining a liquid curable resin and a catalyst or curing agent; spraying or brushing a second thin layer of the resin matrix on top of the cured resin matrix; introducing a thin substrate into the mold to contact the surface of the second layer of resin matrix; curing the resin matrix so that the resin matrix is bonded to the thin substrate by curing to create the bonded composite. The bonded composite can be removed from the mold and subjected to a post-curing process such as heat. The bonded composite can be further treated to expose the metal or stone particles in the exposed surface of the composite article.

Alternately, the process of fabricating the composite comprises the steps of combining a liquid resin curable by heat or heat and pressure and metal or stone particles; spraying or brushing a thin layer of the resin matrix into a mold or onto the surface of a thin substrate; introducing the thin substrate into the mold such that the resin matrix in the mold contacts the substrate or the resin matrix on the substrate contacts the mold; curing the resin matrix by introducing heat or heat and pressure so that the resin matrix is bonded to the thin substrate by curing to create the bonded composite. The bonded composite can be removed from the mold and further treated to expose the metal or stone particles in the exposed surface of the composite article.

The process may further include the step of incorporating floatable particles into the resin matrix and locating, prior to curing, the floatable particles near the surface of the resin matrix that is opposite the resin matrix surface to which

particles are migrating. Thus, the floatable particles will migrate to the surface of the resin matrix that is adjacent to the substrate surface to which the resin matrix will bond. The floatable particles can reduce the amount of resin needed which can make the composite piece lighter and can assist in reducing warpage.

The bonded composite can be further treated to expose the metal or stone particles in the exposed surface of the composite article.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the invention, reference is made to the following detailed description to be read conjunction with the accompanying drawings:

FIG. 1 is a schematic diagram of a mixing vessel into which is fed the main constituents of the resin matrix: a curable liquid resin, particles, and a catalyst.

FIG. 2 is a cross section of a mold containing the resin matrix and a substrate floating on the layer of resin matrix.

FIG. 3 is a cross section of a mold containing the resin matrix and a substrate resting on removable shoulders in the mold.

FIG. 4 is a cross section of a mold containing the resin matrix and a substrate maintained at a fixed height in the resin matrix with spacers (removable shoulders) attached to the backside of the substrate.

FIG. 5 is a cross section of a mold containing a resin matrix and a substrate sized so that the outer edge of the substrate is a distance from the sidewalls of the mold thereby allowing the resin matrix, which is displaced by the substrate, to migrate to the sides of the mold and rise to the top of the sidewalls.

FIG. 6 is a perspective view of a composite article having a raised diamond pattern on its face.

FIG. 7 is a perspective view of a composite piece having a decorative logo on its face.

FIG. 8 is a cross section of a mold containing a thin substrate, resin matrix, and a metal/resin matrix.

FIG. 9 is a cross section of a mold containing a heated pressure plate above and below a mold containing a metal/resin matrix layer and a thin substrate.

DETAILED DESCRIPTION OF THE INVENTION

According to the process of this invention, a resin matrix is prepared and poured into a mold. A substrate is then prepared and introduced into the mold so that a surface of the substrate contacts the resin matrix. Particles in the resin matrix migrate to the outer surface of the resin matrix away from the surface of the substrate that is contacting the resin matrix. After curing of the resin matrix and removing the composite piece from the mold, the resulting composite piece has a thin cured matrix layer that can be post-cured, buffed and polished. If the particles are metal or stone, the outer portion of the resin matrix has a metallic or stone-like appearance. As the resin matrix cures, the inner portion of the resin matrix is bonded integrally and directly by curing to the substrate without the use of an intermediate adhesive and without the need for another fastening composition or mechanism.

Preparing the Resin Matrix

A mixture of a curable liquid resin, a curing agent therefor, and a dispersion of metal or stone particles (or powders) which are more dense than the liquid resin are poured, sprayed, brushed etc. into a mold to create the resin matrix. The particles are permitted to settle in the mold to the lower region of the matrix. The

migration of the particles toward the outer region of the matrix can also be accomplished or assisted by, for example, vibration of the resin matrix in the mold. The particles are concentrated in the outer region before the liquid resin polymerizes and hardens to bind the particles. Thus, the concentrated mass of particles is integrally formed with and bound together by the plastic resin.

Referring to Fig. 1, the first step in manufacturing a composite article such as a floor, wall or building panel in accordance with the invention is to produce a resin matrix 10 in a mixing vessel into which is fed the main constituents of the resin matrix 10, namely, curable liquid resin 14, catalyst 16, and metal or stone particles or powder 18. The resin matrix 10 is formed by mixing the ingredients with a mixing device 20.

The first constituent is a curable liquid resin 10, the second is metal or stone particles or powder 18, and the third is a catalyst 16 or curing agent to cause the liquid resin to polymerize and harden at a predetermined rate. Generally, the catalyst 16 is not added until the liquid resin 10 and the particles 18 are thoroughly intermixed and are about to enter the mold. Otherwise, curing may take place prematurely in the mixing vessel 12.

The concentration of particles relative to the concentration of the liquid resin in the resin matrix is kept high so that the particles quickly settle to the lower region of the resin matrix. This also improves the appearance of the resultant composite piece by greatly reducing print-through which could occur with a smaller amount of particles in a thin cured matrix layer or the substrate. The higher concentration of particles also improves the resistance to warpage in the cured matrix in the composite article. The amount of particles added to the resin matrix is based on a number of factors, for example, the geometry of the piece being cast, the thickness

of the cured matrix layer, the desired appearance and the type of substrate being used. In this sense, the weight of particles utilized should be sufficient to provide a metallic or stone-like appearance to the cured matrix surface once it is buffed. It should also be sufficient to adequately cover the substrate surface to avoid print-through which would destroy the perception that the article is metal or stone. In addition to providing an adequate concentration of particles in the resin matrix, sufficient time should be provided for the metal particles to settle to the surface of the mold in order to avoid print-through. Also helpful is the use of resilient mold materials which flex under the pressure exerted by the substrate.

Typically, the ratio of the amount, by weight, of the metal or stone particles to curable liquid resin in the resin matrix may be from about nine parts particles to one part liquid resin (9:1) to about one part particles to one part liquid resin (1:1). Preferred weight ratios of the constituents of the resin matrix are from about two parts particles to about one part liquid resin (2:1) to about one and one-half parts metal or stone particles to about one part liquid resin (1.5:1). Another preferable ratio is about from about four parts particles to about one part liquid resin (4:1).

Metal particles utilized in the invention are those which would produce a decorative effect such as particles of bronze, pewter, copper, brass, steel, tin, iron or aluminum. Powdered metals such as B-406 Bronze or C-118 Copper produced by U.S. Bronze may be utilized. Particles size will be determined by the surface appearance desired in the finished article. To obtain the appearance of solid metal, particle size should be small enough so that the appearance of the object will be that of solid metal but large enough and of sufficient density so the metal particles will sink in the curable liquid resin to one surface of the resin matrix. Typically, particles in the range of about less than -60 Taylor mesh and most preferably about

less than -140 Taylor mesh, will be satisfactory. Some preferred particles are in the range of about -60 to -325 Taylor mesh and from -200 to about +300 Taylor mesh. However, coarser or larger particles may be used to impart to the piece a different appearance. Spherical particles are preferred and the metal particles preferably have densities between 4g/cc and 8g/cc.

A stone-like appearance can be imparted to the composite piece by incorporating stone particles instead of metal particles into the resin matrix. Any stone or stone-like material can be utilized to achieve the desired effect. Stone particles having a diameter of up to one millimeter are preferred. Stone particle sizes that are preferred are the same sizes mentioned above for the sizes of metal particles. Examples of stone particles include calcium carbonate, sand, granite, marble, slate, hydrated alumina, mica, cement, stone-like composites, ceramics, glass and other particles which impart a stone-like appearance to the composite piece. Stone and metal particles can be added to the resin matrix to achieve certain decorative effects.

The amount of the metal or stone particles which migrate to the outer (or lower) surface of the resin matrix will be affected by various factors, including but not limited to, viscosity of the liquid resin, production requirements, gel time (cure time), the amount and type of additional fillers in the resin matrix, and the type of metal or stone particles.

Various curable liquid resins can be used in the process especially, monomer resins such as acrylates, methacrylates, styrenes, methylstyrenes, allyls, and diallylphthalates. Other resin systems include unsaturated polyesters, vinyl esters, urethanes and epoxies, phenolics and melamines. The monomers can be used alone or in combination with other liquid monomers.

Specific examples of preferred curable liquid resins are Polylite 32-358, an unsaturated polyester resin monomer manufactured by Reichhold Chemicals, Inc. and containing more than 50% unsaturated polyester resin and less than 50% styrene monomer; Aropol 8520-14 an unsaturated polyester resin manufactured by Ashland Chemical, Inc. and containing 65 to 70% by weight unsaturated resin and about 30% by weight styrene; and Envirez 5310, another unsaturated polyester resin manufactured by Ashland and containing 50 to 55% polyester resin, 25 to 30% ethyleneglycol dimethacrylate and 15 to 20% hydroxethyl methacrylate.

The catalyst or curing agent added to the resin matrix is dependent on the type of resin in the matrix. The amounts of the catalyst used can be varied to produce longer or shorter gel, demold, and cure times. The catalyst can be any suitable catalyst used for curing liquid resins such as methyl ethyl ketone peroxide. The catalyst or curing agent may be an organic peroxide catalyst such as Lupersol DDM-9 manufactured by Elf Atochem North America, Inc., or Hi-Point 90 sold by Witco Corporation. For unsaturated polyesters, the catalysts include methyl ethyl ketone peroxide (MEKP) and benzoyl peroxide (BPO). For epoxies, catalysts include aliphatic amines such as diethylene triamine and diethylene tetramine; aromatic amines such as methphenylene diamine, methylene dianinile, and diamino diphenyl sulfone; catalytic curing agents such as piperidine, boron trifluorideethylamine complex and benzyl dimethylamine; and acid anhydrides such as nadic methyl anhydride, dodecenyl succinic anhydride, hexahydrophthalic anhydride, and alkendic anhydride. Preferred catalysts are aliphatic amines or acid anhydrides. For urethanes, catalysts include diamines and polyols.

A dispersion of floatable particles which are less dense than the curable liquid resin may optionally be incorporated into the resin matrix. The

floatable particles may rise to the upper or inner surface of the resin matrix before the liquid resin cures. As the liquid resin cures and shrinks, the presence of the metal or stone particles at one surface of the object and the floatable particles at the opposing surface of the object reduce the weight of the resin matrix.

The floatable particles include powders, microspheres or other particles which have a density which is less than the density of the curable liquid resin so that a substantial portion of the floatable particles will migrate in the liquid resin to the inner (or upper) surface or the surface of the resin matrix opposite the surface containing the particles. The floatable particles may be in the form of powder such as polyethylene or polypropylene, or hollow microspheres made of, for example, ceramic or glass. The fact that these particles float also ensures that they will not migrate to and mark the metallic or stone-like surface of the object.

The amount of floatable particles which migrate to the surface are preferably about equal in volume to the amount of metal or stone particles migrating to the opposing surface. The volume of floatable particles may vary depending on the type of floatable particles, metal or stone particles, and curable liquid resin utilized.

Specific examples of floatable particles include hollow ceramic microspheres containing up to 5% crystalline silica, hollow aluminum silicate microspheres, inorganic sodium borosilicate microspheres containing amorphous silicon dioxide, organosilicon modified aluminum silicate microspheres, and ceramic microspheres coated with aluminum, copper, or zinc. Other additives can be incorporated into the resin matrix to impart desired properties to the composite piece. The amount of each of these materials added to the resin matrix varies depending upon the effects desired. For example, a fire retardant agent, such as aluminum trihydrate (ATH), can be added to the resin matrix so that when the

composite piece takes the form of floor or wall panels, or other articles used in building construction, the composite piece satisfies stringent architectural, structural and fire code requirements. A promoter can help promote curing of the resin at room temperature or to vary the gel, demold, and cure times of the product and can also act to induce decomposition of the organic peroxide catalyst in polyester resins. Inhibitors, such as Aropol Q 6919, can adjust the curing time of the resin and can prevent premature crosslinking of the monomers in polyester resins. The curing time depends on the type of resin used and the ratio of promoter, catalyst, and/or inhibitor added to the mixture.

Sunscreens are another additive which can be incorporated into the resin matrix to protect objects from the deleterious effects of ultraviolet light. Colorants may be added to modify the final color of the object and the resin matrix, and pigments add a background coloration to the resin matrix and serve to accentuate relief. Sealing wax solutions may be added to seal the resin during curing. Air release agents assist the mixture in releasing air entrapped in mixing. Other additives, such as UV absorbers and vapor suppressants may be included to enhance the physical properties of the composite or to improve the physical handling of the resin matrix. A variety of fillers such as hydrated alumina, glass or ceramic microspheres, elastomers, ceramic and carbon fibers, glass fibers or plastic regrind can be used to improve mechanical properties such as flame retardance, weight, resilience, and strength. The amounts of each of these materials added to the resin matrix varies depending upon the effects desired.

The resin matrix, consisting of a curable liquid resin, metal or stone particles, a catalyst and possibly some additives, is blended in a mixing vessel or drum with a mixing device such as a paint stirrer or with more sophisticated metering

and mixing equipment. A high shear mixer is preferred, but any type of mixer that suspends the metal or stone particles in the resin component for a long enough period of time to cast the matrix without separation of the metal or stone is acceptable. After thoroughly mixing the constituents in the vessel to cause the metal or stone particles to become uniformly dispersed in the curable liquid resin, the resin matrix is poured into a mold having a predetermined size and shape.

Mold Preparation

The resin matrix is generally cast in flexible molds which may be made from a variety of materials including silicone rubber, thermoset polyester, stainless steel, or urethane elastomer. The use of the term "mold" is not intended to imply that it has a particular shape or produces a defined pattern on the composite piece. It is only intended to define an area or
container where the resin matrix can contact the substrate and cure.

Prior to adding the resin matrix, the molds may be cleaned with a cleaning agent such as alcohol and are leveled to ensure consistency in the piece and ensure that the composite article will have an even layer of the resin matrix bonded to it. The molds can optionally be sprayed with mold release so that the composite piece can be readily removed from the mold after hardening.

Once molds of the desired size and shape are prepared, the resin matrix can be dispensed into the mold. Material can be poured into the mold by hand, sprayed into the mold with a spray device or dispensed or injected into the mold by automated means.

Preparing the Substrate for Bonding

The resin matrix is dispensed into the mold and the substrate is placed into the mold so that one surface of the substrate contacts the resin matrix. As

illustrated in Fig. 2, a substrate 24 is laid into the mold 26 and is allowed to float on the layer of resin matrix 22. The substrate 24 is preferably placed into the mold starting on one side and slowly dropping to the opposite side to allow any entrapped air to escape. It is not necessary that the substrate be added after the resin matrix is added to the mold. The resin matrix also can be added simultaneously or after the substrate is introduced.

The substrate is a discrete, separate element of the composite article. The substrate is not substantially saturated throughout the entire body of the substrate with the resin from the resin matrix layer. Rather, the resin matrix is bonded to the surface of the substrate by curing the liquid resin.

As illustrated in Fig. 3, the substrate 24 can rest on removable shoulders 28 in the mold 26 which hold it at the desired height until the curing of the resin matrix 22 is complete. The surface of the substrate that contacts the resin matrix can rest on the removable shoulders. These shoulders can be changed to vary the thickness of the resin matrix layer on the substrate.

As shown in Fig. 4, the depth the substrate 24 is lowered into the mold can also be maintained with spacers (removable shoulders) 34 attached to the backside of the substrate 24 which maintain it at a fixed height in the mold 26. These spacers can also be incorporated directly into the mold. A layer of the resin matrix 22 is poured into the mold 26 to the desired thickness. A substrate 24 is laid into the mold 26 and can rest on removable shoulders 34 in the mold which hold it at the desired height until the curing is complete. The height of these shoulders can be changed to vary thickness of the resin matrix layer on the substrate.

As shown in Fig. 5, the substrate 24 is preferably cut so that it is positioned, preferably 1/16" to 1/4", from the sidewalls 30 of the mold 26. This

allows the resin matrix 22, which is displaced by the substrate 24, to migrate to the sides of the mold and rise to the top of the sidewalls.

The substrate functions to provide structural shape and support for the resin matrix layer. It can be made of any material which will provide suitable structural support for the intended use of the finished product. The substrate is preferably substantially self-supporting in structure apart from the composite article and as part of the composite article. The desired degree of structural support and shape may vary depending upon the intended use of the finished product. Substrates include, but are not limited to, wood, particle board, plywood, medium density fiberboard (MDF), cement board, polyurethane foam, wood laminate, honeycomb (made, for example, of plastic, fiberglass, cardboard, or aluminum), metal, sheet metal, concrete, gypsum board, composites, plastic, hardened fiberglass or any other type of structural architectural product or building panel.

The substrates used in this invention can be of any size or thickness or shape. The thickness, shape, or size of the substrate does not affect the process. Preferred sizes include 4'x 8' and 2' x 2' building panels as well as 36" x 72" and 36" x 96" panels. The thickness of the substrate is from about 1/8" to 2" . It may be preferable, although not required, to sandblast or texture the side of the substrate that will come in contact with the resin matrix in order to improve the bond strength between the substrate and the resin matrix.

In a preferred embodiment of this invention, thin sheets of the composite can be formed. The substrate used to create the laminate-like composite can be any substrate which is thin and flexible. The substrate is generally a discrete, separate element of the composite article and provides support and strength to the resin matrix. Suitable substrates include, but are not limited to, thin sheet metal, thin

wood products (such as MDF), plastic sheets (such as plexiglass), fabric, fiberglass mesh, carbon fiber sheets, polycarbonate sheets, PVC and high pressure laminates. The thickness of the substrate is preferably from .01 inches to .25 inches in thickness to create the thin composites.

The Composite Article

The thickness of the resin matrix on the substrate can be controlled by the amount of resin matrix dispensed into the mold, the depth that the substrate is lowered into the mold, and the amount of additional pressure applied to the substrate. The resin matrix can be of any desired thickness on the substrate. A thin layer of resin matrix on a surface of the substrate reduces warpage and shrinkage problems. For example, a resin matrix having a thickness of about 1/32" to about 1/16" is preferred. A particularly preferable range is from about 1/64" to about 1/16". However, a much thicker resin matrix layer (for example, up to one inch or more) can be used. If a thick resin matrix layer is used, an amount of resin may be placed on the backside of the substrate to balance the shrinkage rates to eliminate or reduce warpage and create a flat, dimensionally stable composite. If resin is applied to the non-decorative side of the panel to balance shrink rates, the addition of floatable particles can be useful in accomplishing this balance with less resin, thereby reducing weight and cost.

Generally, the closer the substrate is to the surface of the mold, the thinner the resin matrix will be on the substrate, and the less resin matrix is needed. Uniform thickness of the resin matrix on the substrate is obtained when the mold is level and the substrate is deposited on a parallel plane to the mold.

Depending upon the substrate density, the substrate may be buoyant in the resin matrix, and float on the resin matrix. Thickness of the resin matrix, which is

typically desired to be thin, can be controlled by pressing down uniformly on the substrate.

Once the resin matrix has cured, the bonded composite can be removed from the mold by using compressed air to break the seal between the panel and the mold and then lifting out the piece by hand or mechanical means.

Due to gravity or some applied force, the metal or stone particles in the resin matrix tend to fall to the bottom surface of the mold leaving a thin layer of particles in the outer layer of the resin matrix. The floatable particles, if present in the matrix, are less dense than the metal or stone particles and tend to remain in the inner portion of the resin matrix, close to the substrate. Simultaneously, the inner layer of the resin matrix will have become more resin rich, allowing the resin in the resin matrix to create a strong bond with the substrate.

Uniform dispersion of the metal or stone particles in the resin matrix produces objects which have a metallic or stone-like surface of substantially uniform thickness. The thickness of the surface required will depend upon the use and desired weight of the final object. For instance, a bronze metal surface formed by the concentrated mass of metal particles may be about 0.30 mm to about 1.0 mm thick for a tile which is about 3.2 mm in thickness, whereas a counter top surface may have an about 0.8 to about 2.0 mm thick metal surface. The hardening time of the matrix is such as to permit the relatively heavy particles to settle by gravity and concentrate in the lower region of the mold before the resin matrix gels. Spray deposition of the resin matrix may impel the particles to the appropriate region of the mold surface. Vibration of the mold can also assist the metal or stone particle fallout.

The thinnest layer of resin matrix on the substrate that provides the finished appearance of solid metal or stone with the least manufacturing

complications is desirable. Smaller amounts of resin matrix provide for less warpage or shrinkage of the resultant composite. Layer thicknesses of between 1/32" and 1/16" are preferred but thicknesses smaller than 1/32" are also appropriate. The thickness can be varied by applying uniform downward force against the substrate, thus forcing resin matrix out from under the substrate and to the sides of the mold.

Once the resin matrix is hardened and the resin matrix is bonded to the substrate, the composite piece is removed from the mold. Gel times vary from about 5 to 60 minutes and demold times vary from about 10 to about 180 minutes depending on the type of resin, the amount of metal or stone particles in the matrix, the amounts and types of additives in the matrix, and the amount of catalyst and promoter used. Generally, demolding can take place about 40 to 50 minutes after casting. Once the resin matrix has cured, the bonded composite can be removed from the mold by any number of methods including using compressed air to break the seal between the panel and the mold and then lifting out by hand or mechanical means. This can be done by slightly lifting one corner of the piece and applying air pressure under it to release it from the mold.

After the composite piece is removed from the mold, it is allowed to reach full cure. Unsaturated polyesters can reach full cure at ambient temperatures in 48 to 72 hours. However, the cure cycle can be accelerated at elevated temperatures ranging from 60°F to 300°F depending upon the resin system and the substrate. Further curing of the composite at elevated temperatures is generally referred to as "post-curing". For a specific unsaturated polyester, gel at 75°F with post-cure at 200°F for two hours is optimal.

The composite can generally be cured at a temperature range of from about 60°F to about 250°F depending on the resin system and the substrate. For a

specific unsaturated polyester, gel at 75°F with post-cure at 200°F for two hours is optimal.

Post-curing can generally be accomplished by heating the piece to about 150°F to 250°F for approximately 1.5 to 2.5 hours, depending upon the resin used.

The result is a bonded composite article which has a resin matrix bonded to a substrate. The resin matrix has an outer face region imparting a metallic look to the article and an inner face region bound to the substrate. The outer face region of the resin matrix is defined by a dense mass of metal particles embedded in plastic which act to bind the metal particles together. If floatable particles are used, they are concentrated in the inner face regions of the resin matrix and are embedded in the plastic which also binds the floatable particles together. The cured resin also binds the inner region of resin matrix to the substrate. The resin running throughout the resin matrix forms a strong bond with the substrate material to form a single, integral composite article.

Buffing and Polishing

Once the composite piece is removed from the mold and the curing process is complete, the outer face of the composite contains a thin, plastic skin covering the metal or stone particles. In order to impart the appearance of metal or stone to the object, the outer face of the piece can be treated, for example, by being treated chemically or by being sandblasted, polished, or buffed, to remove the thin encapsulating layer of polymer from the surface, thus exposing the densely packed metal or stone particles.

The outer face of the composite piece is polished and buffed in any suitable way. A buffing wheel can be used to remove the plastic binder skin and

expose the particles at the face to polishing action to produce a polished metal. The buffing process cuts through the encapsulating layer of resin that is covering the metal or stone layer. This resin layer can be removed by buffing the surface with an aggressive cutting compound applied to a stiff cotton buffing wheel. Cutdown buffing may be done with a wide variety of buff styles, base materials, and buffing compounds. For instance, the cutdown buffing may be done with a 12 inch flannel bias buff at 1750 rpms using Learock 857 bar compound from Lea Manufacturing Co. After buffing, the piece is subjected to a glossing step to brighten the exposed metal or stone layer and put a high shine on the piece. This can be accomplished by using a rouge compound applied to a soft cotton wheel. The 12 inch flannel bias buff at 1750 rpms using Learock 349 E bar compound from Lea Manufacturing Co. will accomplish this task.

Typical buffing and polishing compounds utilized and products sold by the Lea Manufacturing Company of Waterbury, Conn., for fine, medium and heavy cuts. For fine cuts (color), a mix of abrasive, fatty acids and glycerides containing about 5 to 15% chrome(III)oxide and 70 to 80% aluminum oxide may be used. Medium cuts (cut and color) are obtained using a mixture of abrasive, fatty acids, glycerides, petroleum wax/oils and soap containing 1 to 5% ethanol 2.2-iminodi-and 67 to 80% silica dust. A heavy cut (cut down) results from the use of a mix or abrasive, fatty acids, glycerides and petroleum wax/oil containing 10 to 35% silica dust and 38 to 60% tripoli dust. There are a wide range of other products available for metal or stone finishing.

After buffing is completed, the buffing compound residue is removed to provide a clean surface for subsequent adhesion of a clear protective coating, if desired, and to improve and protect the objects's aesthetic qualities. Cleaning may be

accomplished by a variety of methods including pressure washing. Cleaning solutions may be acidic or alkaline. Once the object is clean, it is rinsed free of cleaning solution residue. Deionized water may be used, since it does not contain the calcium or magnesium normally present in the local water supply, and, hence leaves the surface free of water spots. The finished object may be air dried if deionized water is used for the rinse.

The face of the object may be treated in a variety of ways such as applying salt water to impart a patina. To protect the finish, a thin, transparent, adherent plastic coating may be applied such as urethane, wax, or other compatible coating. Alternatively, the exposed face may be permitted to age in an oxidizing atmosphere so as to acquire the tarnish or natural patina of the natural metal.

The clean and dry composite pieces may be covered with a clear protective coating on the outer decorative surface. The coating prevents the surface from tarnishing, and protects it against marring and scratching. Useful as coatings are architectural coatings, powder coatings, enamels, and lacquers. Examples of specific coatings include 202W Baking Lacquer from Agate Lacquer Manufacturing Co., Inc. Coatings may be applied using conventional spray techniques. Once such technique utilizes compressed air in combination with a Model 2001SS spray gun from Binks Manufacturing to coat the outer decorative surface of the object with the baking lacquer. After spraying, the object may be baked in order to accelerate the cure of the coating. Baking temperatures and times range from about 150°F to about 250°F and about 5 to about 90 minutes depending on the coating used. An object coated with the 202W baking lacquer typically is baked at about 175°F for about 45 minutes.

In addition, in order to prevent warpage of the substrate caused by exposure to moisture, the back side of the substrate can be sealed with a laminate or

other waterproofing material. The type of sealant used depends upon the substrate. Standard polyurethane wood sealants can be used to for wood product substrates. A layer of polyester resin or polyurethane can also be poured over the back side to encapsulate and seal the substrate.

In practicing the invention, the inner surface of the bottom wall of the mold may be embossed, etched or otherwise modified to create a decorative pattern on the face of the resultant object. The mold will then contain a negative pattern or impression of whatever the pattern or design of the metal composite surface is to be. Thus, as shown by the wall panel in Fig. 6, the outer face 36 of the resin matrix 22, has a raised diamond pattern on its surface. This surface is not only decorative, but also provides a tread to prevent slipping when walking. One could also emboss a logo on the mold to produce a composite article having a logo on its outer face 38 as shown in Fig. 7.

Additionally, by formulating a resin matrix in two (or more) parts, the first part having one metal or stone, and the second part having another metal or stone, objects may be made which give the appearance of being cast from more than one metal and/or stone. For instance, a pattern along the outer edge of a tile or panel may appear to be brass while a pattern in the inner section of the panel may appear to be bronze.

The composite articles of this invention can be treated in terms of utility, buffing, and cleaning like a solid metal or stone piece.

The composite articles can be formed without the use of support shoulders in the mold. This can be accomplished by pouring or spraying a thin layer of the resin matrix into a mold; waiting a sufficient amount of time for the majority of the metal or stone particles to concentrate on the surface of the mold; and placing the

substrate in the mold before the resin matrix gels. A press or some other force may optionally be applied to the top side of the substrate to cause the bottom side of the substrate to fully contact the resin matrix. After the resin matrix fully hardens, the resultant composite piece is removed from the mold.

Using this technique, small amounts of resin matrix can produce a thin layer of resin matrix on the substrate. In addition, the use of a downward force on the substrate, in combination with resilient molds, allows for a uniform distribution of the resin matrix on the substrate, even if the substrate is slightly warped. Allowing the metal or stone particles to settle in the lower portion of the resin matrix before adding the substrate prevents print-through even when using small amounts of the resin matrix to form a thin layer on the substrate.

The resin matrix can be bonded to discrete surfaces or sides of an object or panel to impart a metallic or stone-like appearance to discrete sides of the object. A board or a building panel having a metallic or stone-like appearance on both surfaces can also be produced using this invention. A substrate is placed in a mold containing a resin matrix including metal and/or stone particles as described above. After the particles drop to the lower surface of the resin matrix and the resin hardens, the composite piece is removed from the mold and flipped over. The substrate is then placed in a mold containing a resin matrix including metal or stone particles so that the backside of the substrate is now in contact with the resin matrix. The metal or stone particles again settle to the lower surface of resin matrix and the resin is cured. The resulting composite piece is completely enveloped in the resin material and has a metallic or stone-like appearance on both side of the building panel.

Advantages

This invention after proper finishing produces a composite piece having a metallic or stone-like outer face which imparts the appearance of a solid metal casting or stone carving. The composites of this invention generally contain very small amounts of a curable liquid resin and metal or stone particles, yet have the appearance of a solid stone or metal piece. A major advantage of these composites is that they give the appearance of tiles, stones, or metals yet can be easily used in construction like a piece of paneling, plywood, particle board, building panels or the like. For example, the boards are easily cut and/or attached with ordinary woodworking equipment, such as screws or nails, to a wall or other surfaces. A solid metal or stone panel, tile or molding would generally be too heavy to easily attach to a wall. Additionally, installation does not require a specialist but can be carried out by a carpenter. The composite pieces have the appearance of solid metal or stone surface yet they possess the same or improved mechanical properties as compared to the substrate material. Depending on the substrate, the composite can be lighter than other board or counter surfacing materials. The composites are particularly useful for walls, countertops, ceilings, trim, furniture, and building panels for the outer face of skyscrapers and buildings.

The composites of this invention can be thinner than conventional building materials, are generally less fragile and are easy to handle. They are easy to store and maintain, are less expensive than solid metal products, and can be readily cut to conform to space requirements. The substrate may be glued, nailed or otherwise attached to a wall or floor the same manner as wood or plastic. However, the outer surface now has a the hand and appearance of a stone or metal product.

The small amount of the resin matrix required to form a thin layer on a substrate reduces any shrinkage or warpage problems associated with curing.

Another significant advantage is that the resin adheres directly to the substrate which eliminates the need for any intermediate adhesive, glue or other mastic. Furthermore, the composite boards are resilient, durable, and shatterproof, and are relatively inexpensive in comparison to traditional metal or stone materials.

Another advantage of this invention is its appearance in comparison to similar objects having a metallic glaze. The glazed object has a shiny appearance which mitigates against its visual acceptance as being truly metallic in nature, whereas an object according to this invention has a soft metallic glow, contains real metals, and in time, can acquire a natural patina which is lacking in a glazed object.

Moreover, this invention allows for the in mold capture of graphic detail, relief patterns, and designs.

The process for manufacture of these composite pieces lends itself well to automation. One possible configuration might be a conveyor-type rubber mold moving at a predetermined speed. Spray applicators could be set to apply the resin matrix to the mold at specified times. After a short gel time, the substrate can be laid onto the metal layer. Depending on the type of substrate being used, this can also be a continuous process. Once the bonding is complete the continuous mold would move to the demolding station where the mold would roll under the conveyor, and the bonded composite panel would be separated and prepared for post-curing, grinding, buffing etc.

Another automated configuration might include a conveyor belt having molds and substrate laid in the molds maintained at desired heights by removable shoulders or spacers. The resin matrix may be injected into the area between the mold and the substrate by any means of automated injection. These automated configurations may also include a computer which controls, for example, the

movement of the conveyor belt, the height of the substrate in the mold, and the amount and timing of the introduction of the resin matrix. Furthermore, the composites of this invention may advantageously be manufactured into a flexible, continuous sheet or roll.

The composite pieces and objects described in this application are by no means the only ones which can be produced using this invention. It is possible to form many types of products for use inside and outdoors. As example only and not intended to be an exhaustive list, the invention may be used for interior products such as wall and floor panels and tiles, counter top surfaces, desk tops, table tops, furniture components, trim, decorative brackets, panels, shelves and the like. In products used outdoors, it may be utilized for doors, roof tiles, and outer facings of buildings. By modifying the ingredients of the resin matrix, the object formulated can be adapted for a particular use. For example, if the object is intended for outdoor use, the resin must be suitable for that purpose.

EXAMPLES

Some preferred embodiments of this invention will be further described in the examples detailed below.

Example 1 Typical Formulation for Resin Matrix

Material Component	Parts per hundred resin (phr)
Unsaturated polyester	100.00
Inorganic filler (hydrated alumina)	50.00
Metal Powder	40.00
Methyl ethyl ketone peroxide	1.25

Example 2 Manufacture of Composites

Material Component	Grams
Unsaturated polyester	372.00
Inorganic filler such as hydrated alumina	309.00
Metal powder	648.00
Methyl ethyl ketone peroxide	4.65

Casting

The above ingredients were power mixed for three minutes using a high shear mixing blade. One sixteenth inch of resin matrix was then poured into three 12x12x1/4" molds, each having a different surface texture. Different substrates were used in each mold--particle board in mold #1, rigid honeycomb in mold #2, and a cement tile backer board in mold #3. After a short time (about 2 to 3 minutes) to allow a good portion of the metal to gravitate to the mold surface thereby creating a dense layer of metal particles, the substrate was laid into each mold before the metal matrix began to cure. This allowed the bonding between the resin matrix and the substrate to take place. Uniform downward pressure was applied to the substrate to force the resin matrix out from under the substrate, thus achieving a thin resin matrix layer. Rubber shoulders were placed in the mold to insure the 1/16th" metal layer. In mold curing was complete approximately one hour after the substrate was inserted.

Demolding

The demolding process was accomplished by using compressed air to break the seal between the composite and the mold. The bonded composite was then lifted out of the mold.

Post-Curing

A post-curing process was applied to accelerate the final curing and get maximum strength and hardness. Post-curing was accomplished by placing the composite articles (panels) in an oven at 200°F for two hours.

Cut-Down Buffing

In cut-down buffing, an encapsulating layer of polymer was removed to expose the densely packed layer of metal particles bound by resin. A buffing machine with oscillating buffs and liquid cutting compound was used to complete this process.

Color/Gloss Buffing

In color buffing, the exposed metal layer was further finished to provide a high polish or shine. Color buffing was accomplished using the same buffing machine as the cut-down operation, however, different compound and buffs were required.

Cleaning

Cleaning was accomplished by washing the face of each panel with a sponge and a heated, alkaline, aqueous solution and then spraying each piece with a high pressure water spray. The purpose of the cleaning step was to remove buffing compound residues in preparation for coating the parts with an organic clearcoat.

Coating

Once the metal layer was exposed, the outer surface was protected with a coating to prevent surface oxidation. These composite panels were coated with a two part acrylic polyurethane using conventional automotive refinishing methods to protect the surface from oxidation and chemical attack.

Test Results

Test results indicated that each substrate and resin matrix layer bonded equally as well. The buffed surface of the composite articles (panels) showed no defects. The strength of the panels was increased relative to the strength of a the substrate and the thickness of the resin matrix layer. The weight of each panel was easily altered depending on the type of substrate used.

Thin composites

In another embodiment of this invention, thin sheets of the composite can be formed. These thin composites can be used independently as an architectural or decorative product or can be used as a laminate to be attached to another substrate. When preparing these thin sheets of composite material, the substrate can be imbedded into the resin matrix or can bond by curing to one surface of the resin matrix.

In order to make this thin composite sheet, a resin matrix containing a curable liquid resin, metal or stone particles and a catalyst is prepared as described above. Generally, the catalyst is not added until the liquid resin and the particles are thoroughly intermixed and are about to enter the mold. Otherwise, curing may take place prematurely in the mixing vessel. A thin layer of the resin matrix is then placed into a mold and allowed to harden (cure). A small amount (a thin layer) of a curable liquid resin (of the same or a different type than the resin in the resin matrix) is then mixed with catalyst or curing agent and added on top of the hardened resin matrix. A thin, flexible substrate is then introduced into the mold so that a surface of the substrate contacts the resin. Optionally, a layer of curable liquid resin is added to the backside of the substrate so that the substrate is embedded in the resin.

Alternately, a resin matrix containing a single-component liquid resin curable by heat or heat and pressure, and metal or stone particles is prepared.

Generally, heat or heat and pressure is not applied until the particles are thoroughly intermixed with the liquid resin and introduced into the mold. Otherwise, curing may take place prematurely in the mixing vessel. A press equipped with heat transfer plates is preheated along with the mold. To speed the process, the thin substrate may also be preheated. A thin layer of metal/resin matrix is applied to the surface of the mold or to one surface of the thin substrate. The substrate is placed in the mold such that there is contact between the metal/resin matrix, the mold surface, and the thin substrate. A heat transfer plate is placed on top of the thin substrate and the press is closed to make contact with the heat transfer plate. Even heat is applied until such time as the resin cures. Once the resin has cured, the thin composite is removed from the mold. Subsequent finishing of the metal/resin surface reveals a bright metal layer which embodies the texture of the mold and which resembles solid metal.

After curing of the resin matrix and removing the composite from the mold, the composite may optionally be post-cured. The outer surface of the resulting composite sheet (laminate) is then buffed and polished to impart a metallic or stone-like appearance to the composite.

Optionally, weight can be applied to the substrate or a press can be used to drive out entrapped air, to fully wet the surface of the substrate, and to minimize the thickness of the adhesive resin layer.

The amount of particles and liquid resin used to form the resin matrix is dependent on a number of factors, for example, the size and geometry of the sheet being cast, the thickness of the cured matrix layer and the desired appearance and the type of substrate being used. Preferable amounts are one (1) gram metal particles per square inch and .34 to .35 grams resin per square inch. The types of curable liquid

resins, the types and sizes of the metal and stone particles, and the suitable catalysts for use in the resin matrix are described above.

The concentration of metal particles relative to the concentration of the liquid resin in the resin matrix is kept high to avoid print through and to improve the metallic or stone-like appearance of the sheet. Typically, the ratio of the amount, by weight, of the metal or stone particles to curable liquid resin in the matrix may be from about nine parts particles to one part liquid resin (9:1) to about one part particles to one part liquid resin (1:1).

Other additives, such as those described above, can also be incorporated into the resin matrix to impart desired properties to the thin composite sheet.

Because the composite sheet or laminate is designed to be thin, a small amount (thin layer) of the resin matrix is added to the mold. Generally, the closer the substrate is to the surface of the mold, the thinner the resin matrix will be on the substrate, and the less resin matrix is needed. The matrix can be introduced into the mold in any suitable way, including pouring, spraying, or brushing the matrix into the mold.

The substrate used to create the laminate-like composite can be any substrate which is thin and flexible. The substrate is generally a discrete, separate element of the composite article and provides support and strength to the resin matrix. Suitable substrates include, but are not limited to, thin sheet metal, thin wood products (such as MDF), plastic sheets (such as plexiglass), fabric, fiberglass mesh, carbon fiber sheets, polycarbonate sheets, PVC and high pressure laminate.

The substrates used in this embodiment can be of any size, shape or thickness, but preferably are less than 1/16 inch thick. The substrate is preferably

between .01 inches and .25 inches thick. The use of the composite as a laminate or a laminate-like substance requires that the substrate be as thin as possible while still providing support for the resultant product. The desired thickness and rigidity of the substrate may vary depending upon the intended use of the finished product.

The substrate can be substantially saturated throughout the entire body of the substrate with resin from the resin matrix layer or the substrate can be surrounded by resin by the introduction of additional resin on the back side of the substrate. Alternatively, the resin matrix can be bonded by curing to one surface of the substrate so that only one surface of the substrate is in contact with the resin matrix.

The thickness of the composite can be from 1/32 inch to 3 inches, preferably from .025 inch to .3125 inch, depending on the thickness of the substrate and the amount of resin matrix bonded to the substrate.

Once the composite is removed from the mold and the curing process is complete, the outer face of the composite can be treated, for example, by being treated chemically or by being sandblasted, polished, or buffed as described above, to remove the thin encapsulating layer of polymer from the surface, thus exposing the densely packed metal or stone particles.

As an example, thin composites, less than 1/16 inch thick, have been manufactured using fiberglass mesh as the substrate. After the resin matrix was prepared, sprayed in a mold, and allowed to harden, a thin layer of liquid resin was placed on top of the hardened resin matrix. A thin fiberglass mesh substrate was then introduced into the mold, followed by a thin layer of resin. The composite was removed from the mold and was buffed and polished to impart a metallic or stone-like appearance to the sheet. The resulting product was a thin (less than 1/16 inch)

decorative, architectural product that could be used independently or used as a laminate (bonded to a suitable substrate). These thin composite products can be made into any size sheet or panel or can be made in the form of a continuous roll. A significant advantage of these thin composites is that they can be used like any high pressure laminate, i.e., they can be post-formed or rolled etc.

Thin Composite Example 1

In one embodiment of the invention, a 30" x 96" x 0.042" thin composite was formed from the following:

Stage 1:

- 750 g of unsaturated polyester resin (Reichhold Polylite 32-138)
- 9 g of promoter solution (cobalt naphthenate 6%, Ashland Chemical Co.)
- 3000 g of metal particles (tin powder, 140 Tin, AcuPowder International, LLC)
- 15 g of peroxide catalyst (Lupersol DDM-9, methyl ethyl ketone peroxide, Atochem North America, Inc.)
- One 30" x 96" x 0.026" high pressure laminate balance sheet (Formica Corporation)

Stage 2:

- 1200 g of unsaturated polyester resin (Reichhold Polylite 32-138)
- 14.4 g of promoter solution (cobalt naphthenate 6%, Ashland Chemical Co.)
- 24 g of peroxide catalyst (Lupersol DDM-9, methyl ethyl ketone peroxide, Atochem North America, Inc.)

A resin matrix was formed by dispensing the polyester resin, promoter solution, and metal particles into a mixing container wherein they were blended to form a consistent mixture. Then the peroxide catalyst was added and thoroughly

dispersed. In this case the mixing container served as the feed container for a cup gun (Model ES G100, as purchased through FRP Supply, Inc.). The resin matrix was sprayed at 90 psi into a textured RTV silicone mold to form a thin, even layer of metal particles and resin. The resin matrix was allowed to harden.

Hardening (curing) of the metal/resin matrix can be accelerated by applying heat. Both convection and infrared heat sources are effective.

Metal to resin ratios of 9:1 are possible depending upon metal particle size and resin viscosity. Spray application of a thin layer of the resin matrix along with high metal to resin ratios allow for high concentrations of metal on the surface of the mold. This surface will become the decorative surface of the thin composite. Dense concentrations of metal particles on this surface translate to a brighter metal finish that more closely resembles a solid metal surface.

Spray application could be accomplished using a gel coat system such as manufactured by Binks, Poly-Craft, Venus-Gusmer, or Glas-Craft.

A second resin matrix was formed by dispensing the polyester resin and promoter solution into a mixing container wherein they were blended to evenly disperse the promoter in the resin. Then the peroxide catalyst was added and thoroughly dispersed. Again, the mixing container served as the feed container for a cup gun. The resin matrix was sprayed at 90 psi on top of the metal/resin matrix to form a thin, even layer of catalyzed resin. The purpose of the second resin layer is to bond the metal/resin matrix to the substrate.

Spray application could be accomplished using a gel coat system such as manufactured by Binks, Poly-Craft, Venus-Gusmer, or Glas-Craft.

While the second resin layer was still wet, a thin substrate (a high pressure laminate balance sheet) was placed in the mold such that it came in contact

with the second resin layer. A 30" x 96" x ¾" sheet of particle board was placed on top of the balance sheet. Twelve 100 pound weights were evenly distributed and placed on top of the particle board, beginning in the center and working out towards each end. The purpose of the weights is to force out any entrapped air in the second resin layer to ensure complete coverage of the balance sheet.

Removal of entrapped air could be accomplished by use of a press such as those used in the high pressure decorative laminate industry or by use of vacuum bagging techniques such as those used in the boat building or composite tooling industries.

The second resin matrix was allowed to cure for eight hours. Then the thin composite was removed from the mold. Curing of the composite can be accelerated by applying heat. Convection and infrared heat sources are effective.

Figure 8 is an illustration of this process showing a mold containing a metal/resin matrix, a resin matrix, and a thin substrate.

The resulting thin composite had an overall thickness of 0.042", with a metal/resin layer of 0.016". It was flexible such that it could be rolled to form a 12" diameter roll. Buffing of the metal/resin surface revealed a bright metal finish with the appearance of solid metal. The metal surface exhibited the texture of the RTV silicone mold.

The resulting thin composite can be used like a high pressure decorative laminate. For instance, in creating a counter top, high pressure decorative laminates are bonded to the particle board, plywood, or MDF with contact cement. Because the surface of the composite to be bonded to the counter substrate is the same as that of high pressure decorative laminates such as Formica® laminates manufactured by Formica Corporation or Pionite® laminates manufactured by

Pioneer Plastics Corporation, it can be bonded using the same adhesives as for Formica® or Pionite®. Composites made with 0.026" thick high pressure laminate balance sheet as the substrate and measuring 0.043" in overall thickness were post-formed and laminated to a standard particle board back splash. Post-forming was accomplished over an outside radius of ¾" and an inside radius of ¼". Post-forming of the thin composite was accomplished by heating the composite with a heat gun and bending the composite to conform to the shape of the back splash while it was in a highly flexible state. This is the same method used to post-form high pressure decorative laminates.

Thin Composite Example 2

In another embodiment of the invention, a thin composite was formed from the following:

- 25 g liquid resin curable by heat or heat and pressure (phenol formaldehyde copolymer, Neste Resins Corp.)
- 100 g metal particles (Tin powder 140 Tin, AcuPowder International)
- A 3-7/8" x 3-7/8" x 0.026" high pressure laminate balance sheet (purchased at retail, Formica Corporation)
- A mold made of RTV silicone (Rhodorsil RTV-585, Rhone-Poulenc)

Tin powder was mixed with liquid phenol formaldehyde copolymer to form a resin matrix. A thin, even layer of the resin matrix was applied by foam brush to a thin piece of balance sheet, a high pressure laminate material typically used for laminating to the bottom surface of counter tops surfaced with high pressure decorative laminates such as those manufactured by Formica Corporation or Pioneer Plastics Corporation to prevent warping of the counter top. The balance sheet was placed resin side down into a preheated RTV silicone mold such that the resin matrix

contacted the surface of the mold. A preheated heat transfer plate was placed on top of the balance sheet. The mold containing the resin matrix-coated balance sheet and heat transfer plate was placed in a preheated vulcanizing press equipped with heat transfer plates on top and bottom. The press was closed such that the top press plate contacted the heat transfer plate which was on top of the balance sheet in the mold. The press was allowed to remain in this position for 45 minutes at a temperature of approximately 245°F, after which time the vulcanizing press was opened and the mold removed. The heat transfer plate was removed from the top of the balance sheet and the balance sheet was removed from the mold. This is illustrated in Figure 9 which shows a cross section of a mold with a metal/resin matrix and a thin substrate. A heat transfer plate is above the substrate and heat pressure plates are located above and below the mold.

The resulting composite consisted of a polymerized layer of phenol formaldehyde copolymer and tin powder bonded by heat and pressure to a thin layer of balance sheet. The composite picked up the surface detail of the mold. Subsequently, the composite was buffed to expose a bright, densely packed layer of tin particles bound by phenolic resin, and having the appearance of solid metal.

Liquid resins with viscosities up to 4,000 centipoise are appropriate, although viscosities of less than 300 centipoise are preferable to allow for higher filler loading.

While there has been shown and described some preferred embodiments of this invention, it will be appreciated that this disclosure is for the purpose of illustration and various omissions, changes and modifications may be made without departing from the essential spirit or scope of the invention as set forth in the claims

What is claimed is:

1. A process for creating a thin composite article, comprising the steps of:

a) combining a curable liquid resin, a catalyst or curing agent, and metal or stone particles to form a resin matrix;

b) contacting a thin, flexible substrate, which has a surface, and the resin matrix so that the surface of the substrate is in contact with an inner surface of the resin matrix;

c) forming a concentrated mass of the metal or stone particles on an outer surface of the resin matrix by migration of the metal or stone particles to the outer surface of the resin matrix before curing of the resin matrix; and

d) curing the resin matrix to bond the inner surface of the resin matrix to the surface of the thin substrate and to fix the position of the migrated metal or stone particles to create the article.

2. The process as claimed in claim 1, further comprising the step of treating the outer surface of the article to impart a metallic or stone-like appearance to the article.

3. The process as claimed in claim 1, further comprising the step of post-curing the article.

4. The process as claimed in claim 2, wherein the metal or stone particles are about less than -60 Taylor mesh in size.

5. The process as claimed in claim 3, wherein the article is post-cured by subjecting the article to a temperature of about 150° to 250° F.

6. The process as claimed in claim 3, further comprising the step of treating the outer surface of the article to impart a metallic or stone-like appearance to the article.

7. The process as claimed in claim 1, wherein the metal particles are selected from the group consisting of bronze, steal, tin, copper, aluminum, pewter and brass.

8. The process as claimed in claim 1, wherein the curable liquid resin is selected from the group consisting of an unsaturated polyester, a vinyl ester, a urethane, an acrylate, a methacrylate, a styrene, a methylstyrene, phenolic, melamine, an epoxy, an allyl and a diallylphthalate.

9. The process as claimed in claim 1, wherein the substrate provides structural shape and support for the resin matrix layer.

10. The process as claimed in claim 1, wherein the substrate is selected from the group consisting of thin sheet metal, thin wood products, plastic sheets, fabric, fiberglass mesh, carbon fiber sheets, polycarbonate sheets, PVC and high pressure laminate.

11. The process as claimed in claim 1, wherein the stone particles are selected from the group consisting of calcium carbonate, sand, granite, marble, slate, hydrated alumina, mica, cement, ceramics, stone-like composites, and glass.

12. The process as claimed in claim 1, wherein the substrate provides structural shape and support for the resin matrix layer and is selected from the group consisting of thin sheet metal, thin wood products, plastic sheets, fabric, fiberglass mesh, carbon fiber sheets, polycarbonate sheets, PVC and high pressure laminate; wherein the curable liquid resin is selected from the group consisting of an unsaturated polyester, a vinyl ester, a urethane, an epoxy, phenolic, melamine, an acrylate, a methacrylate, a styrene, a methylstyrene, an allyl and a diallylphthalates; wherein the metal particles are selected from the group consisting of bronze, copper, aluminum, pewter, steel, tin, and brass; and wherein the stone particles are selected from the group consisting of calcium carbonate, sand, granite, marble, slate, hydrated alumina, mica, cement, ceramics, stone-like composites, and glass.

13. The process as claimed in claim 1, wherein the amount, by weight, of the stone and metal particles in the resin matrix is sufficient to provide a metallic or stone-like appearance to the surface of the article.

14. The process as claimed in claim 4, wherein the amount, by weight, of the stone and metal particles in the resin matrix is sufficient to provide a metallic or stone-like appearance to the surface of the article.

15. The process as claimed in claim 12, wherein the amount, by weight, of the stone and metal particles in the resin matrix is sufficient to provide a metallic or stone-like appearance to the surface of the article.

16. The process as claimed in claim 1, wherein the ratio of amount, by weight, of the metal or stone particles to curable liquid resin in the resin matrix is from about nine parts metal or stone particles to one part curable liquid resin to about one part metal or stone particles to one part curable liquid resin.

17. The process as claimed in claim 4, wherein the ratio of amount, by weight, of the metal or stone particles to curable liquid resin in the resin matrix is from about nine parts metal or stone particles to one part curable liquid resin to about one part metal or stone particles to one part curable liquid resin.

18. The process as claimed in claim 12, wherein the ratio of amount, by weight, of the metal or stone particles to curable liquid resin in the resin matrix is from about nine parts metal or stone particles to one part curable liquid resin to about one part metal or stone particles to one part curable liquid resin.

19. A process for creating a thin composite article comprising:

a) combining a curable liquid resin, a catalyst or curing agent and metal or stone particles to form a resin matrix;

b) applying a thin layer of the resin matrix to a mold such that the outer surface of the resin matrix is in contact with the mold;

c) contacting a thin, flexible substrate, which has a surface, and the resin matrix so that the surface of the substrate is in contact with the inner surface of resin matrix;

d) forming a concentrated mass of the metal or stone particles on an outer surface of the resin matrix by migration of the metal or stone particles to the outer surface of the resin matrix before curing of the resin matrix; and

e) curing the resin matrix to bond the inner surface of the resin matrix to the surface of the thin substrate and to fix the position of the migrated metal or stone particles to create the thin composite article.

20. A process for creating a thin composite article comprising the steps of:

a) combining a liquid curable resin, a catalyst or curing agent, and metal or stone particles to form a resin matrix;

b) applying a thin layer of the resin matrix into a mold;

c) forming a concentrated mass of metal or stone particles on the surface of the mold;

d) curing the resin matrix to fix the position of the migrated metal or stone particles;

e) applying a thin layer of a curable liquid resin and a catalyst or curing agent on the cured resin matrix;

f) contacting a thin, flexible substrate, which has a surface, and the curable liquid resin so that the surface of the thin substrate is in contact with the curable liquid resin; and

g) curing the liquid resin layer to bond the curable liquid resin layer in the surface of the thin substrate to create the thin composite article.

21. The process as claimed in claim 1, wherein the thin substrate is from .01 to .25 inches in thickness.

22. The process as claimed in claim 21, wherein the thin substrate is from .01 to .25 inches in thickness.

23. The process as claimed in claim 22, wherein the thin substrate is from .01 to .25 inches in thickness.

24. The process as claimed in claim 1, further comprising the step of applying a downward force on the thin, flexible substrate to cause the surface of the substrate to fully contact the resin matrix before curing the resin matrix.

25. A thin composite article comprising a thin, flexible substrate, said substrate having a surface, and a cured plastic resin having a first surface and a second surface of a concentrated mass of metal or stone particles, the cured plastic resin cured to bond the first surface of the cured plastic resin to the surface of the thin substrate and to fix the concentrated mass of metal or stone particles in the second surface of the cured plastic resin.

26. The article as claimed in claim 25, wherein the resin matrix further comprises an additive selected from the group consisting of a fire retardant agent, a promoter, an inhibitor, a sunscreen, a colorant, a pigment, a sealing wax solution, an air release agent, a UV absorbent, a vapor suppressant, and a filler.

27. The article as in claim 25, wherein the outer metallic or stone-like surface of the resin matrix is treated to impart a metallic or stone-like appearance to the article.

28. The article as claimed in claim 25, wherein the metal particles are selected from the group consisting of bronze, copper, aluminum, pewter, steel, tin and brass.

29. The article as claimed in claim 25, wherein the stone particles are selected from the group consisting of calcium carbonate, sand, granite, marble, slate, hydrated alumina, mica, cement, ceramics, stone-like composites, and glass.

30. The article as claimed in claim 25, wherein the curable liquid resin is selected from the group consisting of an unsaturated polyester, a vinyl ester, a urethane, an acrylate, a methacrylate, a styrene, a methylstyrene, melamine, phenolic, an epoxy, an allyl and a diallylphthalate.

31. The article as claimed in claim 25, wherein the thin, flexible substrate is selected from the group consisting of thin sheet metal, thin wood products, plastic sheets, fabric, fiberglass mesh, carbon fiber sheets, polycarbonate sheets, PVC and high pressure laminate.

32. The article as claimed in claim 25, wherein the thin, flexible substrate is selected from the group consisting of thin sheet metal, thin wood products, plastic

sheets, fabric, fiberglass mesh, carbon fiber sheets, polycarbonate sheets, PVC and high pressure laminate; wherein the curable liquid resin is selected from the group consisting of an unsaturated polyester, a vinyl ester, a urethane, an acrylate, a methacrylate, melamine, phenolic, a styrene, a methylstyrene, an epoxy, an allyl, and a diallylphthalate; wherein the metal particles are selected from the group consisting of bronze, copper, aluminum, steel, tin, pewter, and brass; and wherein the stone particles are selected from the group consisting of calcium carbonate, sand, granite, marble, slate, hydrated alumina, mica, cement, ceramics, stone-like composites, and glass.

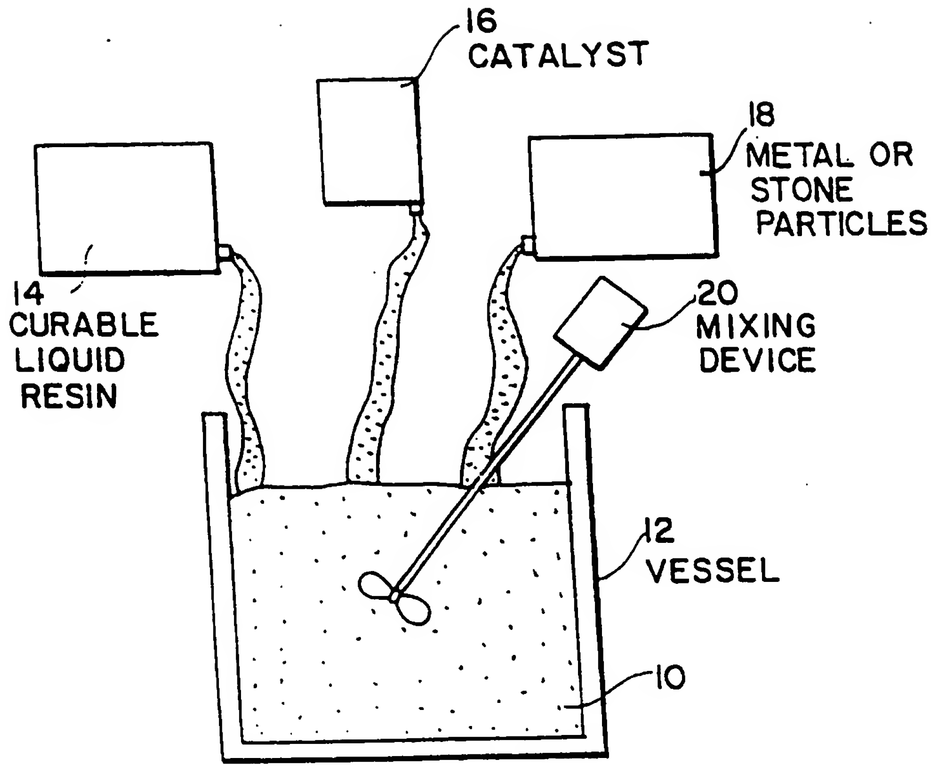
33. The article as claimed in claim 25, wherein the metal or stone particles are about less than -60 Taylor mesh in size.

34. The article as claimed in claim 25, wherein the ratio of amount, by weight, of the metal or stone particles to curable liquid resin in the resin matrix is from about nine parts metal or stone particles to about one part curable liquid resin to about one part metal or stone particles to about one part curable liquid resin.

35. The article as claimed in claim 25, wherein the outer metallic or stone-like surface is coated with a clear protective coating.

36. The article as claimed in claim 25, wherein the surface of the substrate opposite the resin matrix is sealed within a laminate or water proofing material to prevent warpage of the article.

37. A thin composite article which comprises a resin matrix bound by curing to a surface of a thin, flexible substrate, said substrate being structurally, substantially self-supporting, said resin matrix having an outer surface of a concentrated mass of metal or stone particles integrally formed with and bound together by the cured resin and having an inner surface, also integrally formed with and bound together by the cured resin to the surface of the thin, flexible substrate.



COMPOSITE RESIN MIXING

FIG. 1

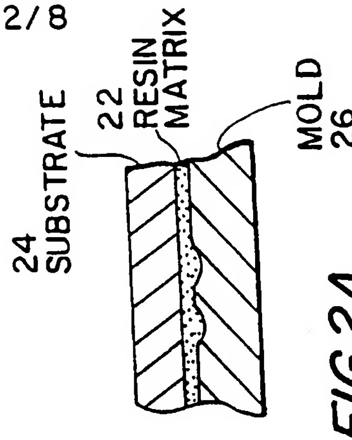

24 SUBSTRATE
22 RESIN MATRIX
MOLD 26

FIG.2A

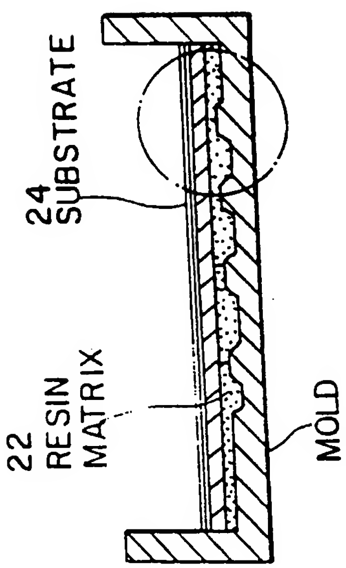

24 SUBSTRATE
22 RESIN MATRIX
MOLD 26

FIG.2

3/8

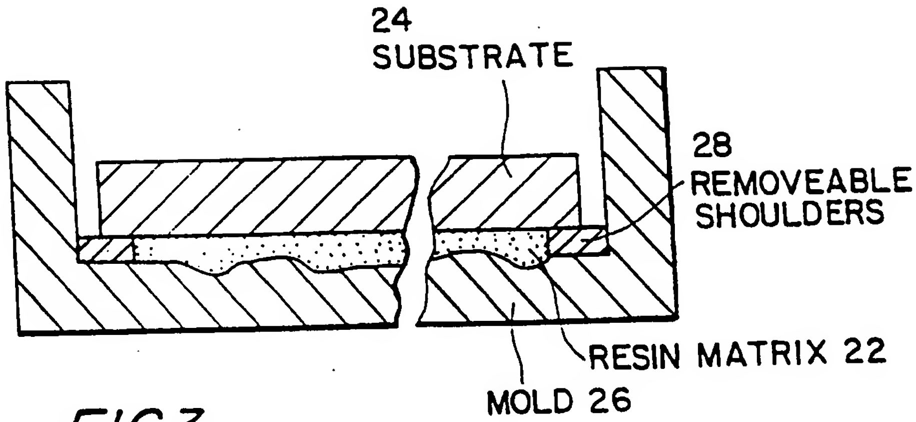

24
SUBSTRATE
28
REMOVEABLE
SHOULDERS
RESIN MATRIX 22
MOLD 26

FIG.3

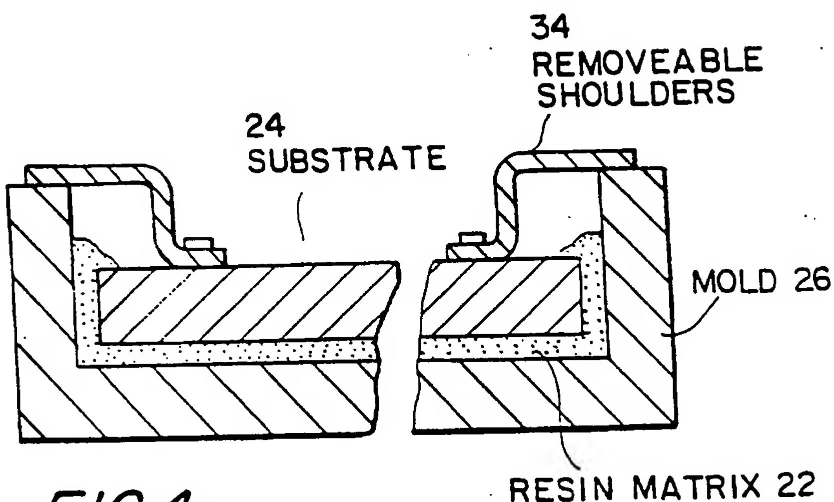

34
REMOVEABLE
SHOULDERS
24
SUBSTRATE
MOLD 26
RESIN MATRIX 22

FIG.4

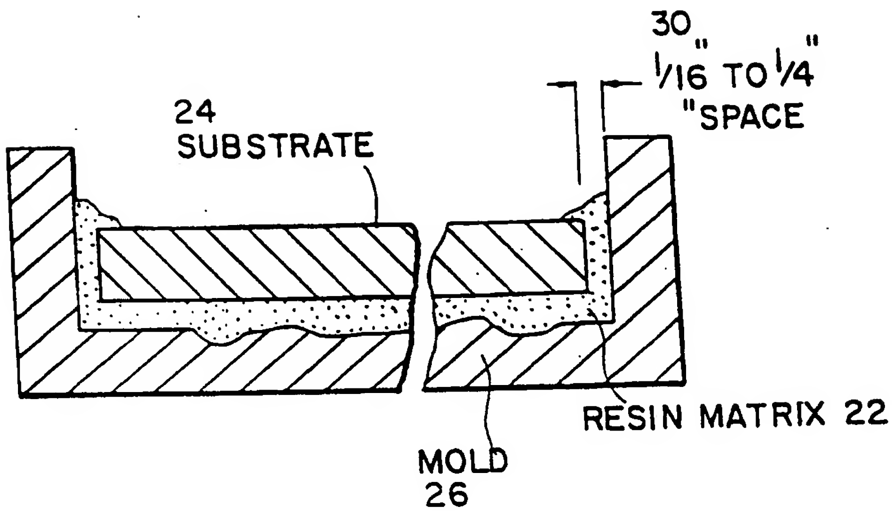


FIG. 5

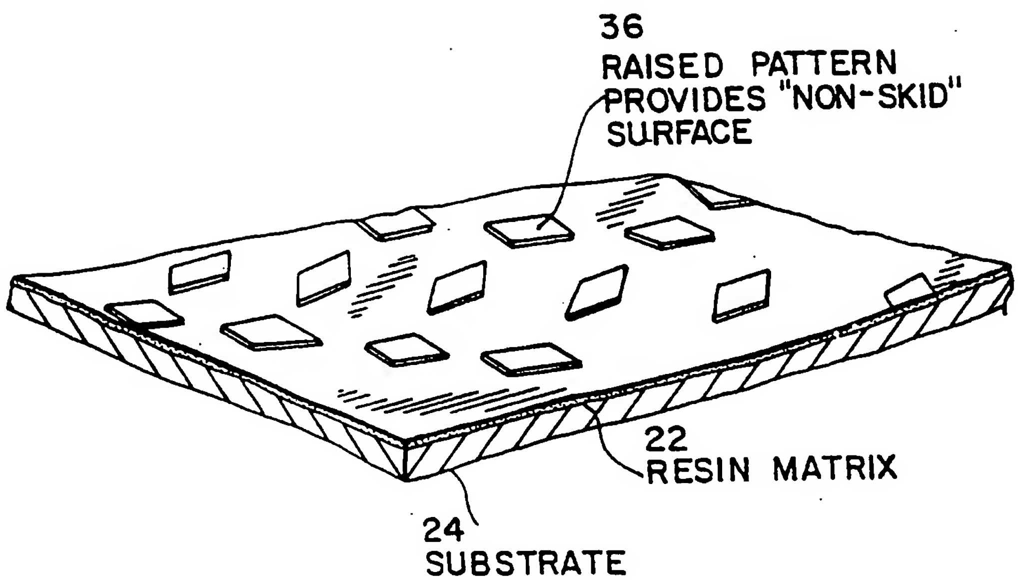

36
RAISED PATTERN
PROVIDES "NON-SKID"
SURFACE
22
RESIN MATRIX
24
SUBSTRATE

FIG.6

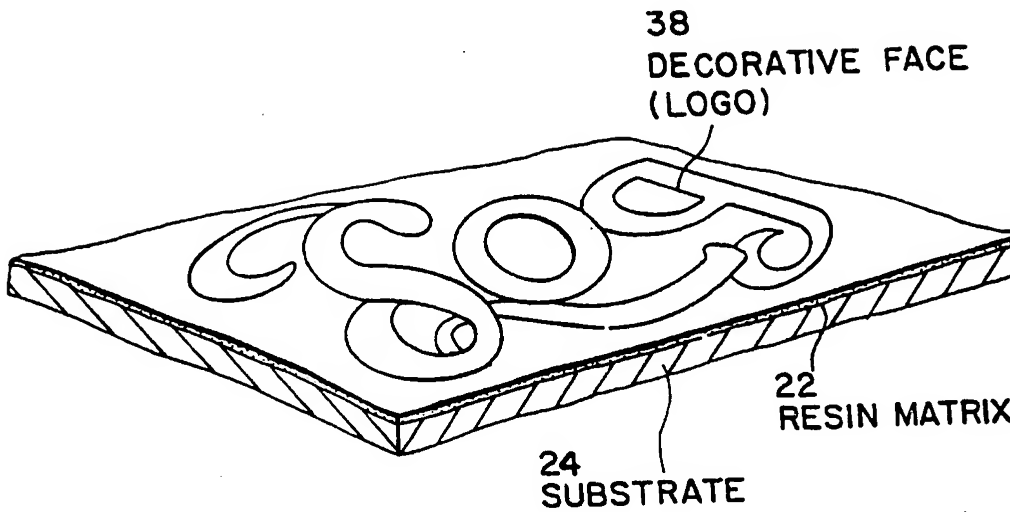


FIG.7

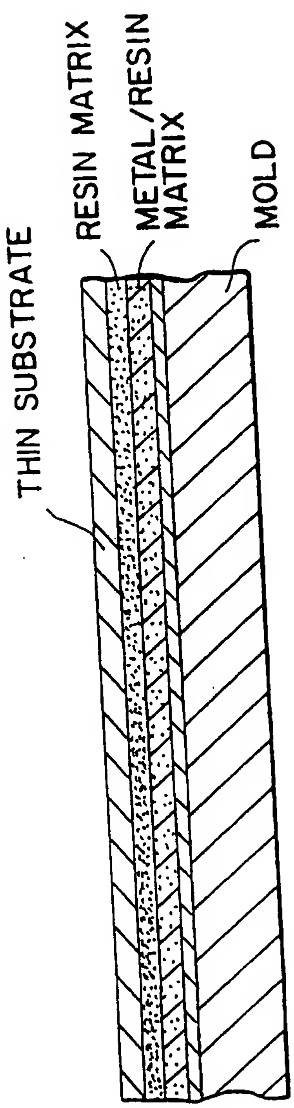


FIG.8

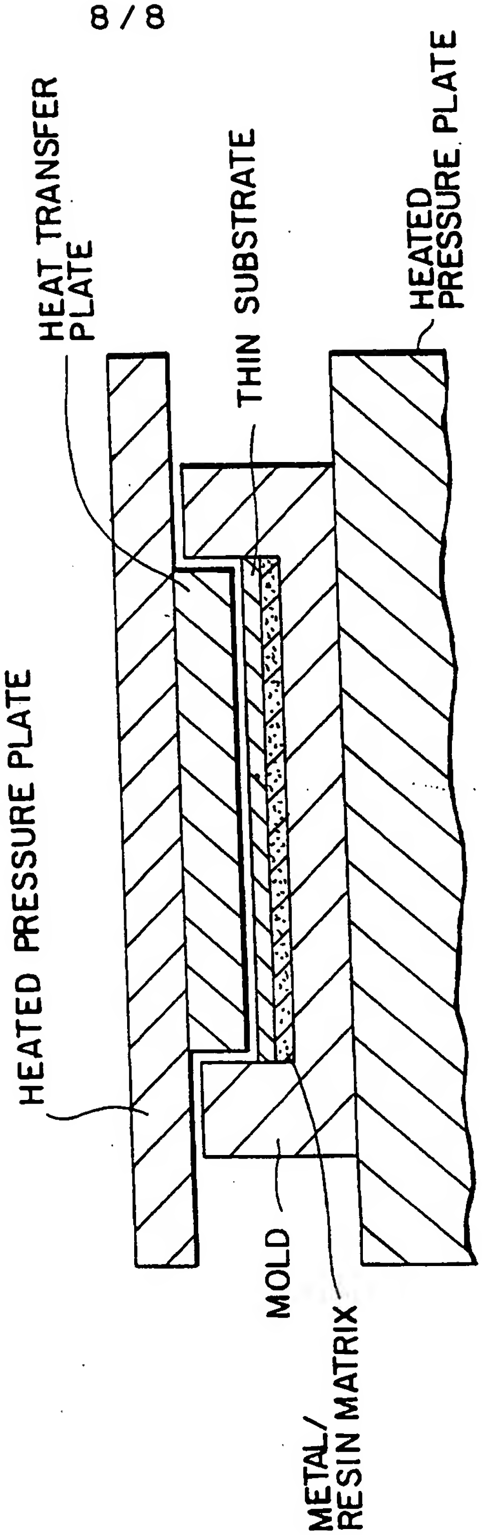

HEAT TRANSFER
PLATE
THIN SUBSTRATE
HEATED
PRESSURE PLATE
HEATED PRESSURE PLATE
MOLD
METAL/
RESIN MATRIX

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/20998

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08J 9/32, C08K 3/40, B27N 3/00
US CL : 524/440, 156/62.2
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/440, 156/62.2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,615,963 A [JOHNASSON et al] 26 October 1971 (26-10-71), column 1, line 41; column 2, lines 23-24, lines 28-33, lines 41-44, lines 49-51.	1, 4, 8-11 19, 21-25, 31,37
Y	US 5,177,124 A [QUESTEL et al] 05 January 1993 (05-01-93), column 4, 39-40, line 45; column 5, 53-61; column 6, lines 38-42, lines 58-61; column8, lines 48-54; column10, lines 7-11, lines 29-33, lines 45-48; column 12, lines 40-47, lines 48-50; column 13, lines 12-14; column 14, lines 30-34.	1-2, 7-8, 12-18, 20 26-28, 30, 32-36
Y	US 5,422,391 A [INOUE] 06 June 1995 (06-06-95), column 5, lines 19-28; column 10, lines 17-22, lines 38-42.	1,4, 6, 11,26, 29

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
18 DECEMBER 1998

Date of mailing of the international search report
14 JAN 1999

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
LING-SIU CHOI
Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/20998

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/20998

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

STN search terms: curable liquid resin, curing agent or catalyst, setted particle (metal or stone), substrate or molding.
APS earch terms: (1) binder, settled particles, panel or panels.; (2) stone, binder, appearance, architecture.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

GroupI, claim(s)1-19, 21-24, 25-37, drawn to a first process of bonding a resin to a substrate, and the resulting article.

Group II, claim(s) 20, drawn to a second process of bonding a resin to a substrate.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I is drawn to a process having a specified series of steps for bonding a resin layer to a substrate in a single step, and the article made from said process. Group II is drawn to a second process wherein a two-step process for bonding a resin to a substrate in which a different series of steps are utilized.